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TITLE: PRODUCTION OF HIGH CORROSION RESISTANT ZIRCONIUM
ALLOY

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ABSTRACT:

PURPOSE: To produce a Zr alloy having excellent corrosion resistance in a high temp. water and high temp. steam environment, at the time of subjecting a Zr alloy stock having a specified compsn. increased in the content of Fe to solution treatment and executing hot working or the like, by executing heat treatment in an α phase region in accordance with the working under specified conditions.

CONSTITUTION: A Zr alloy stock contg., by weight, 0.4 to 1.7% Sn, 0.25 to 0.75%

Fe, 0.05 to 0.30% Cr, 0 to 0.10% Ni and 0 to 1.0% Nb is subjected to solution treatment and is thereafter subjected to hot working and/or cold working. At this time, heat treatment in an α phase region for the purpose of softening before and after the hot working and cold working and stress relieving after the cold working is executed in the range in which, at the time of defining the amt. of heat to be inputted as the heat treating parameter A_i of the formula [A_i , t_i and T_i respectively denote the heat treating parameter in the heat treating stage of the (i) th, the heat treating time (hr) and the heat treating temp. (K) and R denotes gas constant (cal/mol.K)], the total

value σ_{Ai} of each heat treating parameter satisfies
 8.5×10^{-16} to 2.1×10^{-14} .

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DETAILED DESCRIPTION

[Detailed description]

[0001]

[Field of the Invention] this invention relates to the manufacture technique of the zirconium alloy which has the corrosion resistance which was excellent in high temperature hot water or the high-temperature-steam environment used for the nuclear fuel covering spool of a nuclear power plant etc.

[0002]

[Prior art] As configuration components, such as a nuclear fuel covering spool of the reactor which cools a reactor core with water, the parvus zirconium is used compared with the atomic nucleus of others [absorption cross section / to a thermal neutron]. Especially, a zircaloy -4 (ASTM B [353], UNS No.R60804) is put in practical use by the pressurized water reactor (PWR), and the zircaloy -2 (ASTM B [353], UNS No.R60802) is put in practical use by the boiling water reactor (BWR). These zirconium alloys have the corrosion resistance which was excellent in making Sn, Fe, Cr, and nickel of a minute amount contain in high temperature hot water or the high-temperature-steam environment.

[0003] However, high burnup-ization of a nuclear fuel is planned in the specific gravity of the nuclear power generation as a source in recent years of an electric power supply increasing for more efficient power generation. In connection with it, a raise in anti-corrosion more than the former and reinforcement are desired also to the configuration component of reactors, such as a nuclear fuel covering spool.

[0004] The amount of Sn is made lower than the zirconium alloy specified in the Provisional-Publication-No. 213629 [63 to] official report by ASTM specification. The technique of making high corrosion resistance attaining by specifying the total quantity of Sn, Fe, and Cr in a Provisional-Publication-No. 270360 [61 to] official report The technique of raising corrosion resistance by performing an annealing on the conditions on which heat treatment parameter A (it is equivalent to σ_{Ai} of this invention) exceeds the critical value of 2.3×10^{-14} is indicated by 625 of alpha phase field, - 750 ** between the extrusion process and the cold rolling.

[0005] However, the technique which higher corrosion resistance is demanded and was indicated by the Provisional-Publication-No. 213629 [63 to] official report and the Provisional-Publication-No. 270360 [61 to] official report in the motion of a raise in the burnup of a nuclear fuel was inadequate. Furthermore, since the elevated temperature with the large heat gain of each annealing process and a prolonged annealing are required for the technique indicated by the Provisional-Publication-No. 270360 [61 to] official report, it has the problem of elevation of an energy cost, or a fall of a productivity.

[0006]

[Object of the Invention] this invention is to offer the manufacture technique of the zirconium alloy which has the corrosion resistance which was excellent in high temperature hot water or the high-temperature-steam environment which cancels the above-mentioned trouble and is used for the nuclear fuel covering spool of a nuclear power plant etc.

[0007]

[The means for solving a technical problem] Then, in order to obtain the zirconium alloy which has high corrosion resistance more, as a result of repeating a study, this invention persons' corrosion resistance should improve by considering as Fe content higher than a convention of **ASTM.

[0008] ** When Fe content is raised, it is that the conventional knowledge makes the heat treatment conditions accompanied by a manipulation into the low heat gain by the side of a short time at low temperature conversely, and the product which has good corrosion resistance rather than level conventionally should be obtained.

[0009] The above knowledge is acquired and it came to complete this invention.

[0010] this invention is weight % here. Sn:0.4 - 1.7%, Fe:0.25-0.75%, Cr: 0.05-0.30%, nickel:0 -0.10%, Nb : It faces performing manipulation between solution treatment post heating, and/or cold working using the zirconium-alloy material containing 0 - 1.0%. Heat treatment in alpha phase field accompanied by the manipulation It is the heat treatment parameter A_i of a lower formula about the heat gain in the i -th heat treatment process. When expressed, it is total value σ_{Ai} of the heat gain in each heat treatment process. 8.5×10^{-16} to 2.1×10^{-14} It is the manufacture technique of the high corrosion resistance zirconium alloy performed in the domain.

[0011] $A_i = t_i \exp(-65000 / RT_i)$ A_i : Heat treatment parameter t_i in the heat treatment process of eye i watch : Heat treatment time in the heat treatment process of eye i watch (time)

Ti Heat treatment temperature in the heat treatment process of eye :i watch (K)

R: Gas constant (cal/mol and K)

[0012]

[Operation] Next, this invention is explained in detail.

[0013] First, although composition of the zirconium alloy of this invention is explained, "%" is "weight %" below.

[0014] Sn: In order that 0.4 - 1.7 %Sn may suppress the degradation of corrosion resistance by the nitrogen which is an unescapable impurity, make it contain. Moreover, there is also work which secures a mechanical strength. Sn content At less than 0.4%, a mechanical strength is not securable. On the other hand, if 1.7% is made to exceed and contain, corrosion resistance will be reduced conversely. It followed and the content of Sn was made into 0.4 - 1.7 %.

[0015] Fe: In order that 0.25-0.75%Fe may secure corrosion resistance and a mechanical strength, make it contain. At less than 0.25%, Fe content cannot secure corrosion resistance but becomes inadequate [a mechanical strength]. On the other hand, if Fe content exceeds 0.75%, on the heat treatment conditions of this invention, workability may fall, a surface surface deterioration may occur at the time of cold working, and it may result in a crack. Although it followed and the content of Fe considered as 0.25 - 0.75%, it is desirable to consider as 0.65% or less from the amount which exceeded 0.4% from the point of on-the-strength reservation, and the point of workability reservation.

[0016] Cr: Make 0.05-0.30%Cr contain like Fe for corrosion resistance and on-the-strength reservation. At less than 0.05%, the enhancement effect of corrosion resistance [content / Cr] does not accept. On the other hand, since workability would fall if 0.30% is made to exceed and contain, the content of Cr could be 0.05 - 0.30%.

[0017] nickel: 0 - 0.10%nickel is an element made to contain if needed for the further corrosion-resistant improvement. In order to acquire this effect, considering as 0.005% or more is desirable the case where nickel is made to contain positively. Moreover, in order that there may also be work which absorbs the hydrogen which occurred by corrosion reaction and too much inclusion may affect a mechanical property, the upper limit in the case of making it contain is 0.10%.

[0018] Nb: 0 - 1.0 %Nb is an element made to contain like nickel if needed for the enhancement in the further corrosion resistance. It is desirable, when [0.05% or more of] making it contain positively, in order to acquire the effect. On the other hand, since corrosion resistance and workability would be reduced if 1.0 % is exceeded and contained, the upper limit was made into 1.0 %.

[0019] Next, heat treatment conditions are explained.

[0020] Although the process which manufactures a zirconium alloy from a zirconium-alloy material performs hot working after performing solution treatment first, and cold working of several times is performed after that, heat treatment in alpha phase field is performed for the purpose of malacia before and after hot working or cold working, and ***** after cold working. It heat-treats in alpha phase field for not making the intermetallic compound which exceeded and separated ***** re-****. Moreover, although it changes a little with composition, it is a desirable temperature requirement. It is 560 to 700 degree C. However, what is necessary is just to perform the last annealing performed at the last of a process in the domain of 450 to 500 degree C, since it aims at ***** of a product.

[0021] Furthermore, the heat treatment conditions of this invention are the heat treatment parameter A_i of a lower formula about the heat gain in the i-th heat treatment process in heat treatment in alpha field accompanied by hot working or cold working. When expressed, it is total value σA_i of the heat treatment parameter in each heat treatment process. 8.5×10^{-16} to 2.1×10^{-14} It is required to carry out in the domain.

[0022] $A_i = t_i \exp(-65000 / RT_i)$ A_i : Heat treatment parameter t_i in the heat treatment process of eye i watch : Heat treatment time in the heat treatment process of eye i watch (time)

Ti Heat treatment temperature in the heat treatment process of eye :i watch (K)

R: Gas constant (cal/mol and K)

σA_i 8.5×10^{-16} When it is the following, workability may fall, the surface surface deterioration at the time of cold working may occur, and it may result in a crack. Furthermore, corrosion resistance also falls. On the other hand, σA_i 2.1×10^{-14} Since it becomes an elevated temperature and prolonged heat treatment while corrosion resistance will fall, if it exceeds, elevation of an energy cost and a fall of a productivity will be caused and it is not desirable.

[0023] Moreover, although the total value of each heat gain in the heat treatment process after solution treatment has prescribed the heat treatment conditions of this invention, heat treatment in alpha phase field accompanied by a manipulation is indispensable, and when heat treatment before a manipulation and after a manipulation is omitted and the following manipulation process is performed, a surface surface deterioration and a surface crack generate it at the time of a manipulation.

[0024] Especially the conditions of each heat treatment process are not specified, and should just be heated to alpha phase field. Heat treatment parameter A_i By heat treatment performed between each manipulation process although not limited especially With 1.8×10^{-17} to 5.0×10^{-15} , and the last annealing 3.4×10^{-20} to 6.3×10^{-19} A domain is desirable.

[0025] As mentioned above, the knowledge that corrosion resistance of this invention improves with the conventional elevated temperature and prolonged heat treatment is completely reverse knowledge, and the zirconium alloy excellent in corrosion resistance was able to be obtained in the zirconium alloy which raised Fe content from elegance conventionally by specifying the heat treatment conditions accompanied by the manipulation to a low heat input side conventionally.

[0026] Since the intermetallic compound separated near the grain boundary of alloy base metal is distributed minutely and with high density, the ground is considered because the protected area to oxidation reaction is formed near the grain

boundary.

[0027] Moreover, in the case of a plate, in the case of tubular material, a bar, a wire rod, etc., with hot working and cold working which are said by this invention, the manipulation technique, such as forging, extrusion, and ****, is mentioned for forging, rolling, etc.

[0028]

[Example] Hereafter, the effect of this invention is explained based on an example.

[0029] It has the composition shown in Table 1 with a vacuum melting, casting, and forging. The zirconium-alloy material of 177mmphi was prepared. According to the process which shows the material in Table 2 and 3, the zirconium-alloy spool for nuclear fuel covering spools was manufactured. In addition, hot working of front Naka is a hot extrusion, cold working is a cold rolling, and it is total value sigmaAi of a heat treatment parameter. Each heat gain A1 of processing [of Table 2 and 3] **, - heat treatment **, - A7 It is the total value.

[0030] In order to evaluate the workability of the zirconium-alloy spool manufactured at this process, the surface deterioration on the front face of a spool and the crack occurrence status were observed. Furthermore, from a spool, a sample with a length of 50mm is started, a front face is ground, and it considers as a test piece, and is a test piece. To the inside of a 400-degree C hyperbaric-pressure steam It was exposed for 150 days and the gravimetry of the test piece before and behind an examination performed evaluation of corrosion resistance in quest of cauterization increase in quantity. The result is doubled and shown in Table 1.

[0031]

[Table 1]

表1

試番	合金No	組成 (wt%)					工程	腐食増量 (mg/dm ²)	表面状況	備考
		Sn	Fe	Cr	Ni	Nb				
1	A 1*	1.29	0.21*	0.10	-	-	イ*	137.2	良好	比較例
2							ロ	105.8	"	比較例
3							ハ	106.2	"	比較例
4							ニ	100.7	"	比較例
5							ホ*	100.2	"	従来例
6	A 2	1.29	0.39	0.09	-	-	イ*	98.9	肌荒れ	比較例
7							ロ	94.7	良好	本発明例
8							ハ	95.5	"	本発明例
9							ニ	95.5	"	本発明例
10							ホ*	105.5	"	比較例
11	A 3	1.30	0.61	0.10	-	-	イ*	99.1	割れ	比較例
12							ロ	94.0	良好	本発明例
13							ハ	95.7	"	本発明例
14							ニ	96.0	"	本発明例
15							ホ*	104.9	"	比較例
16							ヘ	95.1	"	本発明例
17							ト	94.6	"	本発明例
18							チ	95.4	"	本発明例
19							リ	94.9	"	本発明例
20							又*	98.7	割れ	比較例
21	A 4*	1.29	0.78*	0.10	-	-	イ*	100.3	割れ	比較例
22							ロ	94.2	肌荒れ	比較例
23							ハ	95.4	"	比較例
24							ニ	95.8	"	比較例
25							ホ*	105.2	"	比較例
26	A 5	0.52	0.45	0.23	-	-	ハ	51.2	良好	本発明例
27							ホ*	66.4	"	比較例
28	A 6*	1.73*	0.45	0.20	-	-	ハ	152.2	良好	比較例
29							ホ*	390.8	"	比較例
30	B 1	1.29	0.39	0.09	0.05	-	ハ	37.5	良好	本発明例
31							ホ*	44.1	"	比較例
32	B 2	1.30	0.61	0.10	1.05	-	ハ	37.2	良好	本発明例
33							ホ*	46.0	"	比較例
34	C 1	1.29	0.39	0.09	-	0.21	ハ	57.4	良好	本発明例
35							ホ*	68.9	"	比較例
36	C 2	1.30	0.61	0.10	-	0.21	ハ	57.6	良好	本発明例
37							ホ*	68.1	"	比較例
38	D 1	1.30	0.61	0.10	0.05	0.21	ハ	30.2	良好	本発明例
39							ホ*	35.1	"	比較例

*は本発明範囲を外れていることを示す。

[0032]

[Table 2]

表2

工程	イ	ロ	ハ	ニ	ホ
溶体化処理	1050℃x1h その後水焼入				
熱処理①	649℃x0.5h ($A_1=2.0 \times 10^{-10}$)				
冷間加工	177mmφ → 80.0mmφx18.75mmt				
熱処理②	649℃x1.5hr ($A_2=5.9 \times 10^{-10}$)				
冷間加工	80.0mmφx18.75mmt → 63.5mmφx10.9mmt				
熱処理③	530℃x2h	580℃x2h	600℃x2h	650℃x2h	730℃x2h
冷間加工	63.5mmφx10.9mmt → 44.4mmφx7.6mmt				
熱処理④	530℃x2h	580℃x2h	600℃x2h	650℃x2h	730℃x2h
冷間加工	44.4mmφx7.6mmt → 25.5mmφx3.5mmt				
熱処理⑤	530℃x2h	580℃x2h	600℃x2h	650℃x2h	730℃x2h
冷間加工	25.5mmφx3.5mmt → 14.6mmφx1.65mmt				
熱処理⑥	530℃x2h	580℃x2h	600℃x2h	650℃x2h	730℃x2h
冷間加工	14.6mmφx1.65mmt → 9.53mmφx0.66mmt				
熱処理⑦	450℃x1.5hr ($A_7=3.4 \times 10^{-20}$)				
ΣA_i	8.0×10^{-10} *	9.6×10^{-10}	1.2×10^{-10}	4.0×10^{-10}	5.5×10^{-14} *
備考	比較例	本発明例	本発明例	本発明例	従来例

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熱処理工程③～⑥の各条件での A_i は下記

加熱温度	時間	A_i
530℃	2h	4.1×10^{-10}
580℃	2h	4.4×10^{-11}
600℃	2h	1.1×10^{-10}
650℃	2h	8.1×10^{-10}
730℃	2h	1.4×10^{-14}

[0033]

[Table 3]

表3

工程	ヘ	ト	チ	リ	ヌ
溶体化処理	1050°Cx1h その後水焼入				
熱処理①	649°Cx0.5h ($A_1=2.0 \times 10^{-16}$)				
熱間加工	177mm ϕ → 80.0mm ϕ x18.75mm				
熱処理②	649°Cx1.5hr ($A_2=5.9 \times 10^{-16}$)				
冷間加工	80.0mm ϕ x18.75mm → 63.5mm ϕ x10.9mm				
熱処理③	730°Cx1h	580°Cx2h	730°Cx1h	650°Cx1h	650°Cx2h
冷間加工	63.5mm ϕ x10.9mm → 44.4mm ϕ x7.6mm				
熱処理④	730°Cx1h	600°Cx2h	650°Cx2h	700°Cx1h	650°Cx2h
冷間加工	44.4mm ϕ x7.6mm → 25.5mm ϕ x3.5mm				
熱処理⑤	700°Cx1h	650°Cx2h	600°Cx2h	700°Cx2h	650°Cx2h
冷間加工	25.5mm ϕ x3.5mm → 14.6mm ϕ x1.65mm				
熱処理⑥	700°Cx1h	730°Cx2h	530°Cx2h	700°Cx0.5h	なし *
冷間加工	14.6mm ϕ x1.65mm → 9.53mm ϕ x0.66mm				
熱処理⑦	450°Cx1.5hr ($A_7=3.4 \times 10^{-20}$)				
ΣA_i	2.0×10^{-14}	1.5×10^{-14}	8.6×10^{-15}	1.0×10^{-14}	3.2×10^{-15}
備考	本発明例	本発明例	本発明例	本発明例	比較例

*は本発明範囲を外れていることを示す

熱処理工程③～⑥の各条件での A_i は下記

加熱温度	時間	A_i	加熱温度	時間	A_i
530°C	2h	4.1×10^{-18}	700°C	0.5h	1.3×10^{-15}
580°C	2h	4.4×10^{-17}		1h	2.5×10^{-15}
600°C	2h	1.1×10^{-16}		2h	5.0×10^{-14}
650°C	1h	4.1×10^{-16}	730°C	1h	6.9×10^{-15}
	2h	8.1×10^{-16}		2h	1.4×10^{-14}

[0034] From Table 1 - 3, the zirconium alloy manufactured on the composition within the limits of this invention and heat treatment conditions shows the result with good corrosion resistance and workability. On the other hand, even if the alloys NoA1 which are the conventional material are the heat treatment conditions of this invention domain, corrosion resistance is falling, and with the alloy NoA4 with Fe content higher than this invention domain, although corrosion resistance is good, the surface deterioration and the crack have occurred on the spool front face after a manipulation. Furthermore, corrosion resistance is falling with the alloy No6 with Sn content higher than this invention domain.

[0035] Moreover, sigma A_i at the time of heat treatment Corrosion resistance and workability are bad and the spool manufactured by process ** lower than this invention domain is sigma A_i . A fall of corrosion resistance [spool / which was manufactured by process ** (the conventional heat gain) higher than this invention domain] is seen. Moreover, the crack had occurred with the spool manufactured by process ** which omitted heat treatment after a manipulation.

[0036] Furthermore, although the corrosion resistance superior to what is not added is shown, when it manufactures by the conventional process **, corrosion resistance is falling by the steel NoB1 which added nickel and Nb as an alloy element, B-2, and C1, C2 and D1.

[0037]

[Effect of the invention] While according to the manufacture technique of this invention the zirconium alloy which has the corrosion resistance which was excellent in high temperature hot water or the high-temperature-steam environment can be manufactured and reinforcement of the structural members for atomic powers, such as a nuclear fuel covering spool, can be attained, heat treatment of a heat treatment parameter lower than the former is attained, and it can contribute not only to a reduction of an energy cost but to the enhancement in a productivity.

[0038]

[Translation done.]